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Photocatalytic Degradation of Phenol Wastewater: Optimization of Photo Fenton Process

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Abstract

Phenolic compounds are classified as hazardous materials that polluted groundwater and surface water resources. The present work have been applied photo- Fenton process for removal of phenolic wastewater, also it concerned with the optimization of the operating parameters that affect the photo-Fenton process. Using the Response Surface Methodology (RSM) to explore the influence of operational variables such as hydrogen peroxide and the iron ion weight ratio, pH, contact time on the removal of phenol. The predicted removal obtained from the model are in a good agreement within the results of experiments with a high correlation regression of 0.993. The expected maximum removal was to be 80.12 % while the experimental results was 81%. The study estimated the influence of [Fe^{2+}/H_2O_2] weigh ratio from 20-60, contact time from 30-90 min and pH range from 2 to 8, at solution containing of 100ppm phenol. A Box–Behnken design was applied to optimize the operating parameters. The graphical response surface and contour plots were employed to determine the optimum conditions. The results showed that the optimized value of the [H_2O_2/ Fe^{2+}] = 40.4, contact time= 55 min, and pH=5.2 giving a reduction efficiency of 80.12%.

Keywords: Photo;Fenton process; Degradation;Response surface Methodology;Phenolic wastewater.

1. Introduction

Water pollution is one of the most important problems in our world that causes a risk to the environment and humans. The increasing human and industrial activities led to more increment on the discharge of wastewater into the water resources. Phenol is an intermediate product; aromatic hydrocarbon oxidation pathway[1]. Phenol obtained from different industrial processes such as insecticides, pesticides, pharmaceutical, refineries, etc., represents the main pollutants of water[2]. Phenolic compounds are considered as toxic matter and its degradation is difficult. The main phenol degradation intermediates are hydroquinone, glycerol, benzoquinone, catechol, resorcinol, maleic acid, oxalic acid, salicylic acid, 1,2,3-benzotriol,muconic acid and formaldehyde [2]. Thus, it is important to develop materials and effective methods that allow the removal of these pollutants from water.

Different methods are applied to overcome this problem. Photocatalysis is a promising technology which is able to remove phenol from water[3]. In the photocatalysis process, a semiconductor material is used to produce chemical species with high reactivity and makes possible the degrading the molecules of the contaminants[4-5].

Optimizing of the parameters that effect on waste water treatment plays a key role towards the success of the Fenton process. Optimization involves changing of one variable (say amount of Fe^{2+}) at a time while fixing all other variables at one level and

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studying the effect of that variable on the response [6-7]. This is an extremely time-consuming, expensive, and complicated process for a multi-variable/parameter system. To overcome this difficulty, a statistical-based technique, which is commonly called the Response Surface Method (RSM) (Montgomery, 1991) [8-9] is used as a powerful experimental design tool for optimizing the most important factors in the Fenton's reagent process.

The Response Surface Methodology (RSM) is a collection of mathematical and statistical techniques that useful for improving and optimizing processes by using many of designed experiments [6]. It is explanation of the variations of the response (i.e. removal or efficiency) as a function of two independent variables at the central value of the other variables, so it lead to minimize the number of experiments that required for decreasing the cost [9].In this study the factors affecting the photo-Fenton process efficiency for the removal of phenol could be optimized and estimated[8]. Using a Box–Behnken experimental design to determine the optimal conditions of three variables, hydrogen peroxide and the iron ion weight ratio, contact time and pH, so this lead to maximize the removal efficiency of phenol from the wastewater.

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Experimental

Materials

Phenol crystals (98% purity) were purchased from Alpha Chemicals. The stock solution was prepared at a concentration of 1000 mg/L and used as the model pollutant. Ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) as the source of Fe (II), sodium hydroxide (NaOH,97%purity) and Sulphuric acid (H_2SO_4,98%purity) were used for pH adjustment. Hydrogen peroxide (20%), all provided by Sigma Company.

Experimental methods

Fenton's Photocatalysis

The photoreactions were happened in a batch reactor. The phenol wastewater flowed through a tubular photoreactor, which was connected with a UV lamp (15W). All studied samples were taken at one point and one time and the feedstock samples were kept in the laboratory in a cool place, which were then homogenized and tested. The Phenol solution was prepared according to the required concentration by adding the required amount of phenol 100 mg in1000mL distilled water then The amount of the photo-Fenton catalyst is added, after that the mixture is agitated at 1200 rpm for 10 minutes. a peristaltic pump connected to the tank was operated at a specific discharge rate so that the pollutant suspension was circulated from the vessel to the tubular photo reactor and again to the vessel and the cycle is repeated. Samples were withdrawn periodically for analysis.

Analysis is run on the turbidity meter for determining the pollutant concentration at the beginning, the end and intermediate time intervals throughout the experiments; thus determining the amount of phenols degraded at different time intervals.

Experimental Design

To observe the effect of the changes on one or more response variables, we should change one or more process factors (or variables) in an experiment. The (statistical) design of experiments is an efficient procedure for planning experiments so that the data obtained can be analyzed to yield valid and objective conclusions. Design of an experiment is considered as a test or a set of tests in which the process inputs (independent variables) are changed and the output response (dependent variables) is observed. The objective of the design of the experiment is to improve its performance (Montgomery, 1991) [8].

RSM was applied to optimize the parameters of the reaction. The design of experiments, regression analysis and the response surfaces were estimated by applying the Statistical Analysis Software System [10].A three-level three-factor Box–Behnken experimental design was chosen to generate the response surface methodological model.

Coding of variable

Applying an appropriate coding transformation of the variable was an important aspect of response-surface analysis. The way the data are coded affects the results of analysis[9,11]. Using a coding method that makes all coded variables in the experiment vary over the same range is a way of giving each predictor an equal share in potentially determining the steepest-ascent path[12]. There are three independent variables, i.e. $[H_2O_2 / Fe^{+2}]_{ratio}$, contact time and pH as X_1, X_2, and X_3, respectively. The ranges of the experimental variables are chosen according to the preliminary tests run earlier. These ranges and levels

are presented in table 1 as coded and un-coded variable.

Table 1. Range and levels of the coded and un-coded variable.

Variable	Symbols		Range and levels		
	un-coded	coded	-1	0	1
$[H_2O_2]/[Fe^{+2}]_{ratio}$	x_1	X_1	20	40	60
Contact time(min)	x_2	X_2	30	60	90
pH	x_3	X_3	2	5	8

Statistical analysis for response surface methodology was been applied either a first-order or a second-order model. In this study the second-order model was applied in response surface methodology because it is very flexible, It is easy to evaluate the parameters By applying the least squares method[13]. Table 2 shows the fifteen experiments that are required to complete the experimental design

Table 2 . Experimental and coded values of the experimental design

Run number	Coded factor values			Experimental values		
	X_1	X_2	X_3	$[H_2O_2]/[Fe^{+2}]_{ratio}$	Contact time(min)	pH
1	1	1	0	20	30	5
2	1	1	0	20	90	5
3	1	1	0	60	30	5
4	1	1	0	60	90	5
5	0	1	1	40	30	2
6	0	1	1	40	30	8
7	0	1	1	40	90	2
8	0	1	1	40	90	8
9	1	0	1	20	60	2
10	1	0	1	60	60	2
11	1	0	1	20	60	8
12	1	0	1	60	60	8
13	0	0	0	40	60	5
14	0	0	0	40	60	5
15	0	0	0	40	60	5

Conducting the experiments according to that design and collecting the data followed by the verification of the predicted data. The data is then statistically analyzed to measure the likely error and give the guidelines to the validity of the results[14].

Results and discussion

Box-Behnken design was applied to estimate the optimum operating variables of the Fenton's reagent in the process of phenol degradation. According to the Box-Behnken design in SAS software, three levels of experiments are required to be conducted for fifteen runs of experiments that are required for a complete set of the experimental design [15]. These experimental design data is a guide to conduct those experiments in the experimental set up for the phenol pollutant wastewater. After the fifteen runs were done, the values of the reduction in concentration are given and the data of that experimental response were introduced again as input is SAS software. Then, SAS software can calculate the predicted response. The values of the predicted and experimental values are shown in table 3.

Table 3. The experimental design and the response function [(Y (%), concentration reduction (%)].

Run number	Response (Y, %)	
	Experimental values	Predicted values
1	14	12
2	9	14
3	19	14
4	11	13
5	40	42
6	42	36
7	26	31
8	38	36
9	50	50
10	10	13
11	10	7
12	45	45
13	81	80
14	79	80
15	80	80

The following second order polynomial equation is obtained from analysis of the data by SAS:

Concentration reduction % = $80.00 + 0.25\ X_1 - 3.87\ X_2 + 1.13\ X_3 - 37.25\ X_1*X_1 - 29.50\ X_2*X_2 - 14.00\ X_3*X_3 - 0.75\ X_1*X_2 + 18.75\ X_1*X_3 + 2.50\ X_2*X_3$

Fig. 1 compares the experimental values in contradiction of the predicted responses of the model in the removal of concentration. These results showed a good agreement between predicted and experimental values. It was detected that the predicted response from the model is in coincidence with the experimental data.

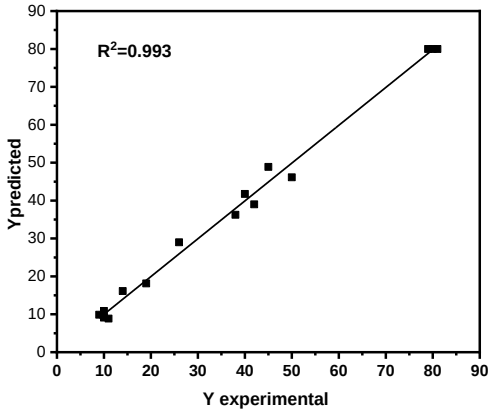

Fig. 1. Values of the predicted versus experimental response.

The relation between the predicted and experimental models is illustrated in Fig. 1 with a correlation coefficient of (R^2= 0.993). The high correlation coefficient (R^2) demonstrates how well the model fits the experimental data (as shown in Fig. 1).

Analysis of variance of model (ANOVA)

The *P* value, *F* ratio, sum of squares and mean square of each factor are presented in Table 4. The aim of this section were to define the optimum condition for maximum removal of phenol. In general, the larger the magnitude of *F* and the smaller the value of *P* (the probability of exceedance of *F*) the more significant is the corresponding coefficient term[16]. The importance of the data is refereed by its *P* value, with values nearer to zero meaning more significance. The model is significant when the *P*-value is less than or equal to 0.05. It prefer that high correlation coefficient (R^2) (as shown in Fig. 1), the model being rejected if the R^2 value is less than 0.8.By fixing one parameter at its zero level.

Table 4 presents a statistical analysis of the data by SAS. The analysis was done by means of the coefficient of correlation (R^2) of the experimental data and by means of Fisher's (*F*) test. The correlation coefficient is a

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measure of the goodness of fit between the model and experimental data. In general, the model is being rejected if the R^2 value is less than 0.8 [17-18]. Thus, the present model is accepted as the R^2 is high (99.3).After the model is accepted the optimum values will be calculated through Mathematical software from the polynomial equation and the values of the optimum variables and the correspondence response are given in table 5.

Table 4. Analysis of variance for the response surface.

Source	DF	SS	MS	*F*	*Pr > F*
X_1	1	0.50	0.50	0.04	0.856
X_2	1	120.13	120.13	8.80	0.031
X_3	1	10.13	10.13	0.74	0.428
X_1*X_1	1	5123.31	5123.31	375.33	0.000
X_2*X_2	1	3213.23	3213.23	235.40	0.000
X_3*X_3	1	723.69	723.69	53.02	0.001
2-Way Interaction	3	1433.50	477.83	35.01	0.001
X_1*X_2	1	2.25	2.25	0.16	0.702
X_1*X_3	1	1406.25	1406.25	103.02	0.000
X_2*X_3	1	25.00	25.00	1.83	0.234

Table 5. Optimum values of the process parameters for maximum efficiency.

Parameter	Optimum value
C% (concentration reduction)	80.12
$[H_2O_2/Fe^{2+}]$ ratio	40.4
Contact time (min)	55
pH	5.2

It is possible to graphically represent the relationship between the percentage concentration removal and the other two independent variables using Minitab 17[19] (Figs. 2 – 4). Minitab 17 software is used to get the surface& contour plot between each two independent variables and the optimum response according to Table 5 and Figs. 2, 3 and 4.

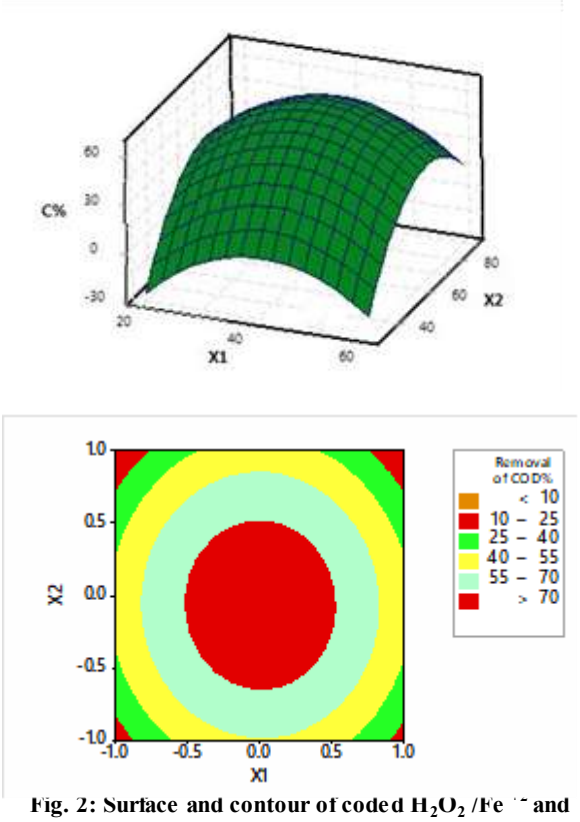

Fig. 2: Surface and contour of coded H_2O_2 /Fe $^{+2}$ and time vs. predicted reduction efficiency

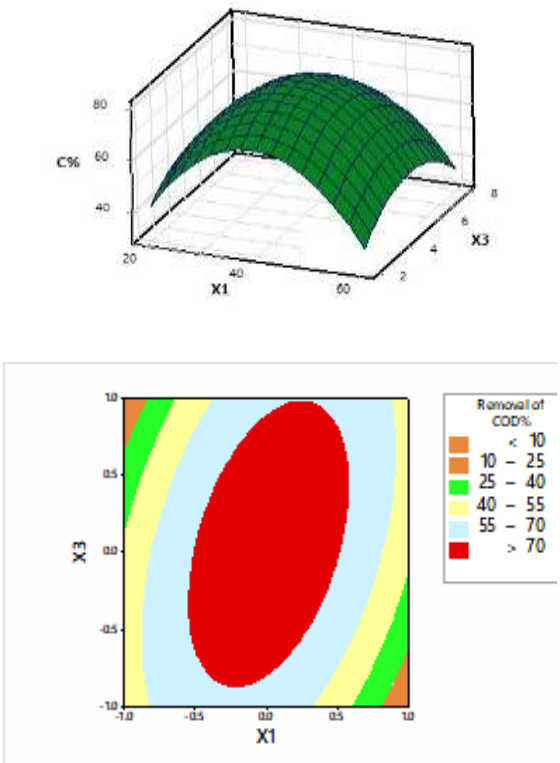

Fig. 3: Surface and contour of coded H_2O_2 /Fe $^{+2}$and pH vs. predicted reduction efficiency

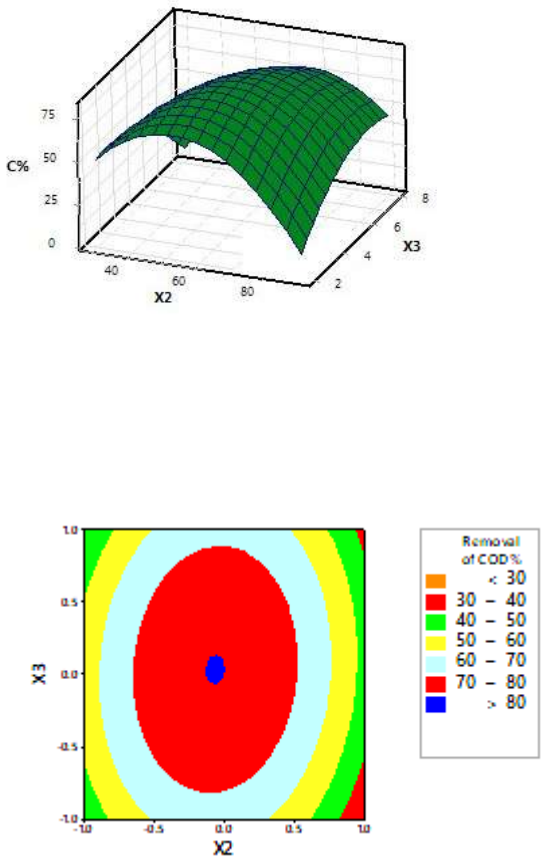

Fig. 4: Surface and contour of coded pH and Contact time vs. predicted reduction efficiency

By using MINITAB 17 (Figs. 2– 4), the optimum values of the selected variables in the photo-Fenton process were obtained using Mathematical software: $[H_2O_2]$ / $[Fe^{2+}]$ = 40.4; contact time = 55min; pH = 5.2 and percentage removal = 80.12%.

From these figures it is observed that the optimized value of $[H_2O_2]$/ $[Fe^{+2}]$ is 40.4. If we reduce this ratio less than that amount, the concentration will not be enough for the mineralization of phenols in waste water and the rate of mineralization slows down and more formation of iron precipitate[20]. This is considered the main disadvantage of the process; due to shading of UV light. While if the ratio increase above 25, this will have an adverse effect on phenol's removal. This can be explained by considering the scavenging effect of hydrogen peroxide on hydroxyl radicals. H_2O_2 may react with OH radical to form oxygen and perhydroxyl radicals and thus decreasing the concentration of free hydroxyl radicals. This phenomenon was observed earlier by Rodriguez [21].

The figures show that the optimized value of pH is 5.2. If higher concentration is used the stream of pollutant becomes more turbid and this will prevent the adsorption of UV irradiation [22], so less mineralization of phenols pollutant will take place.

Model Validation

Three experiments applying were carried at the setting optimal values of the independent factors, to prove the strength of the model that predict the maximum percentage of phenol removal. The average of maximum phenol removal efficiency resulted from the three experiments was 81 %. Good congruence between the experimental and predicted values proves the validity of the model and the presence of an optimal point. From the obtained results ,this study could be proved that the RSM is a useful tool for optimizing the suggested factors to maximize the degradation of phenol.

Conclusions

Using the photo-Fenton process toward degradation of phenols wastewater showed a best results . The response surface methodology design was applied for optimizing the removal capacity of phenols polluted waste water. The high correlation coefficient ($R^2$0.993) indicated that the model was more efficient for calculated the concentration removal as a function of [H_2O_2] / [Fe^{2+}] dosing, time of the reaction and pH dosing. The optimum values led to a percentage phenols degradation of 80.12%.There is a good agreement between the experimental and predicted values of removal efficiency [81-80.12] respectively, so the response surface methodology has proven to be the best technique for optimization.

Conflicts of interest

"There are no conflicts to declare".

Formatting of funding sources

There is no funding resource

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Foremost, I am very thankful that god hasn't let me alone .This is my own work and every think in this work done me

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